NIST-GCR-96-694

POST-FLAME SOOT

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March 1996
Issued June 1996

U.S. Department of Commerce
Michael Kantor, *Secretary*
Technology Administration
Mary L. Good, *Under Secretary for Technology*
National Institute of Standards and Technology
Arati Prabhakar, *Director*

Notice

This report was prepared for the Building and Fire Research Laboratory of the National Institute of Standards and Technology under grant number 70NANB4H1652. The statement and conclusions contained in this report are those of the authors and do not necessarily reflect the views of the National Institute of Standards and Technology or the Building and Fire Research Laboratory.

The smoke agglomerates produced by a co-annular diffusion flame with acetylene fuel were characterized by sampling/microscopy and by light scattering measurements. Particles were sampled at various heights above the flame using both thermophoretic sampling and impaction. Transmission electron microscopy was used for the smaller agglomerates obtained by thermophoretic sampling and optical microscopy was used for analysis of particles as large as .4 mm in diameter collected by impaction. The number of primary spheres was estimated from the projected area of the agglomerate and the primary sphere size. The fractal analysis extended over four orders of magnitude in the radius of gyration - the widest range studied for smokes. The fractal dimension and the prefactor were determined for smoke collected for a range of heights above the flame. The structure factor measurements were performed for angles ranging from 1° to 150° as a function of height and fuel flow. No Guinier regime was observed at a flow rate of 30 ml/min. Modeling results suggest that the slight dip in the structure factor measurements might result from intercluster scattering. A condition for the transition from Brownian agglomeration to gelation is derived.

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Award Number 70NANB4H1652

Final Report

March 1, 1996

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In this final report I include the four previous quarterly reports for the funded year's work and a brief description of work performed subsequent to these reports in the period after September 1, 1995.

Summary of Work Since September 1, 1996

Light Scattering. We have continued to work on understanding the unusual structure factors observed in C_2H_2 in air diffusion flames as shown in Fig. 4 of the Sept. 1995 Quarterly Report. To do this we have simulated aggregation on a computer. Simulations have used a DLCA algorithm in both 2 and 3 dimensions in boxes of 1000x1000 or 100x100x100, respectively. Monomer densities used are in the range of 10^{-4} to $5x10^{-2}$. The whole array is Fourier transformed to yield the structure factor. Examples of our boxes and S(q) are given in Figs. 1 and 2.

The S(q) behavior in Fig. 2 shows at large q the power law, q^{-D_f}, behavior; a Guinier regime related to R_g of the cluster and a Rayleigh regime for $q<R_g^{-1}$. As aggregation proceeds note how a slight minimum occurs in this small q, Rayleigh regime for a monomer density of 10^{-3}. Preliminary results for higher densities show an even bigger dip and peak structure. This is due to intercluster scattering because the intercluster length scale is getting smaller, approaching R_g. It takes monomer-dense systems for this to occur in the q of our experiment but measurements and calculations for our flames show this might explain our results.

Notice also the effects of finite box size on the computer S(q). These finite size effects are still visible at q~10/box size. Our flame is getting quite narrow with $\ell \sim 1mm = 10^3 \mu$ hence $10/\ell \sim 10^{-2}\mu^{-1}$. Our smallest experimental q is $10^{-1}\mu^{-1}$. This is an order of magnitude different but close enough that we should investigate the possibility that our unusual S(q) behavior is due to finite size effects of the flame.

We remark that it has recently been realized that aggregation and spinodal decomposition yield similar S(q) behavior and papers have appeared that attempt to explain this [1-5]. In parallel with our efforts, with flames, we have been able to explain the S(q) scaling behavior of both systems using

simple ideas of light scattering. This explanation appears new and valuable. We also believe the kinetics of spinodal decomposition may be explainable with the Smoluchowski equation. Both these new insights may uncover fertile new ground for research.

Microsecond Photography. We purchased an Oriel xenon flash lamp system that can provide ~μsec, visible light pulses. This apparatus arrived ca. Feb. 10, 1996. Mr. Toby Rush, an honors student in Mechanical Engineering, will work this semester to set up this apparatus and take pictures of large soot in flames as part of an honors project. Thus we are proceeding on my goal of studying very large soot.

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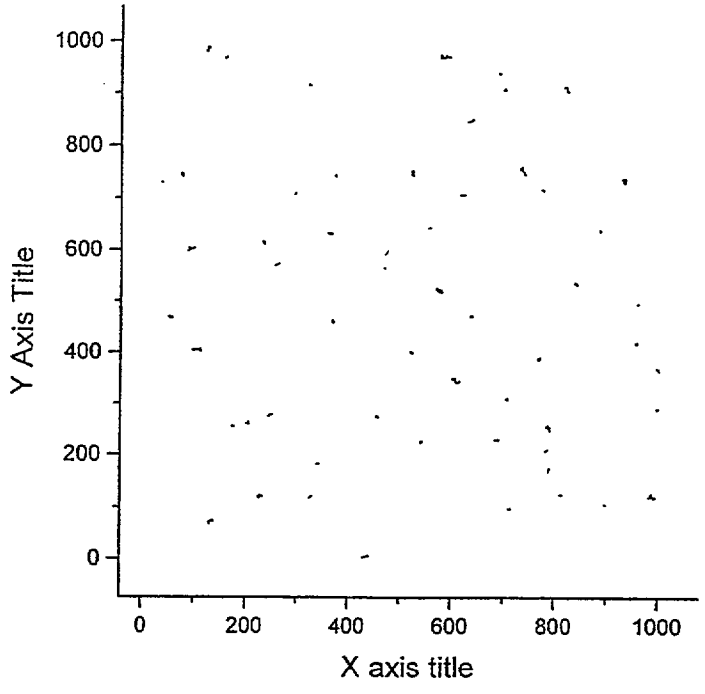

Fig. 1a 1000 Monomers on a 1000x1000 square lattice after 10^8 steps. Clusters have formed. The Fourier transform of this is in Fig. 2, down triangles.

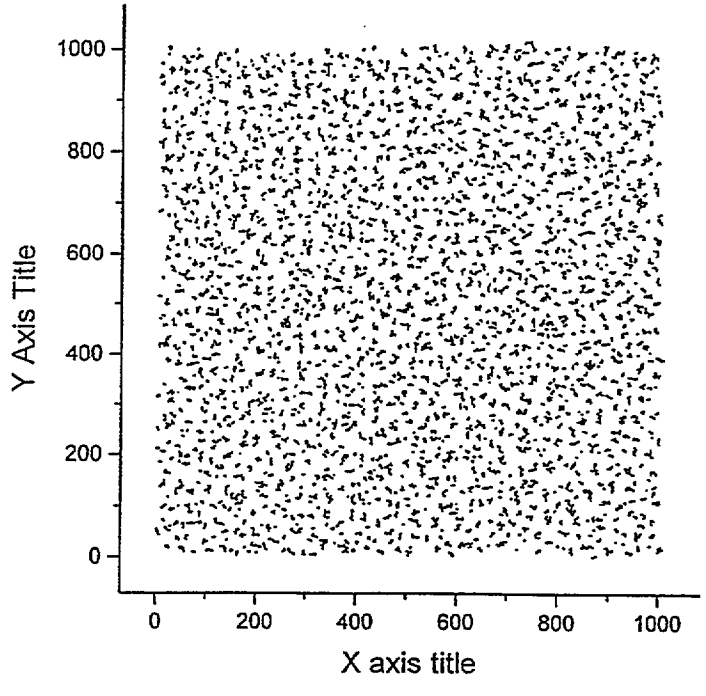

Fig. 1b 50,000 monomers on a 1000x1000 square lattice after $5x10^7$ steps. Note clusters and spaces between clusters are quasi periodic. Fourier transform should show "Fringes."

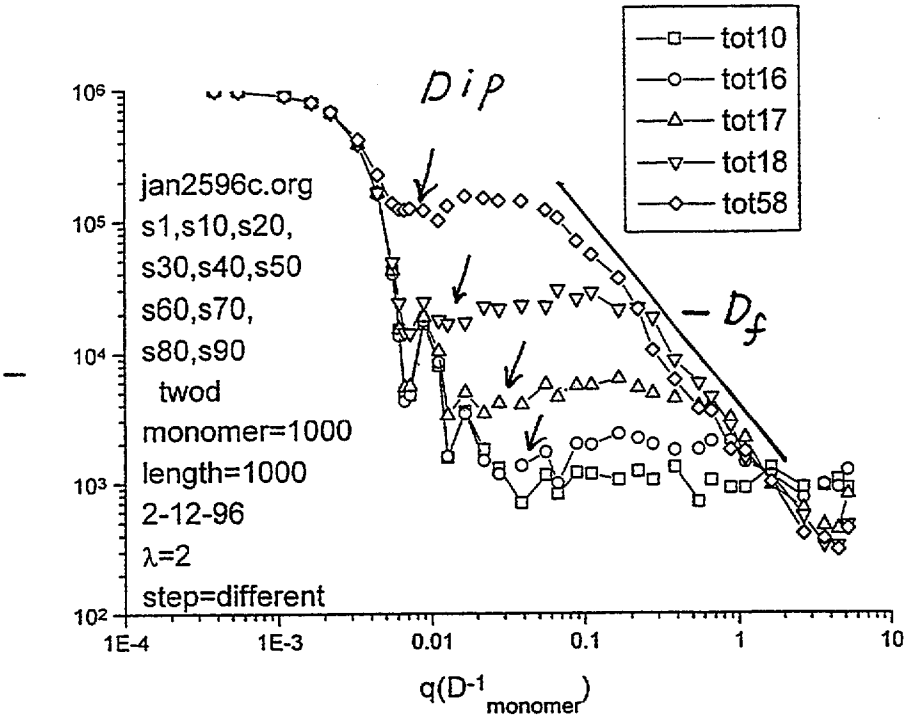

Fig. 2 Scattered intensity versus scattering wavevector for 2D aggregating system of 1000 monomers on a 1000x1000 square lattice at different times.

Post-Flame Soot
Award Number: 70NANB4H1652
Quarterly Report
December 1, 1994

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Good progress was made during this quarter (and the summer proceeding it) on our initial attempts to build diffusion flame burners and collect and characterize soot produced by them with acetylene fuel. The work was done by two undergraduates, Gil Feke, a physics major from Boston University visiting KSU as an NSF REU student, and Greg Brown a recent physics bachelor's degree student from KSU.

I. COANNULAR DIFFUSION BURNER

A. The Burner

A coannular diffusion burner was built based on a burner used by Santoro et al. [1] It consists of an inner brass fuel tube 1/2"O.D. and an outer stainless steel tube 3"O.D. The tubes are cylindrical and coaxial. A screen cap is placed over the top of the fuel tube to keep the flame from going back into the tube. Nitrogen and oxygen were premixed for the air tube. A removable Pyrex glass chimney, 3 1/8"I.D. could be set over the burner. All is mounted on an xyz translation stage. BB's are used as flow randomizers.

B. The Flame

We found the acetylene flame most stable with no air flow in the outer cylinder. Figure 1 shows a qualitative picture of our flame when the flow rate was 0.193 L/min.

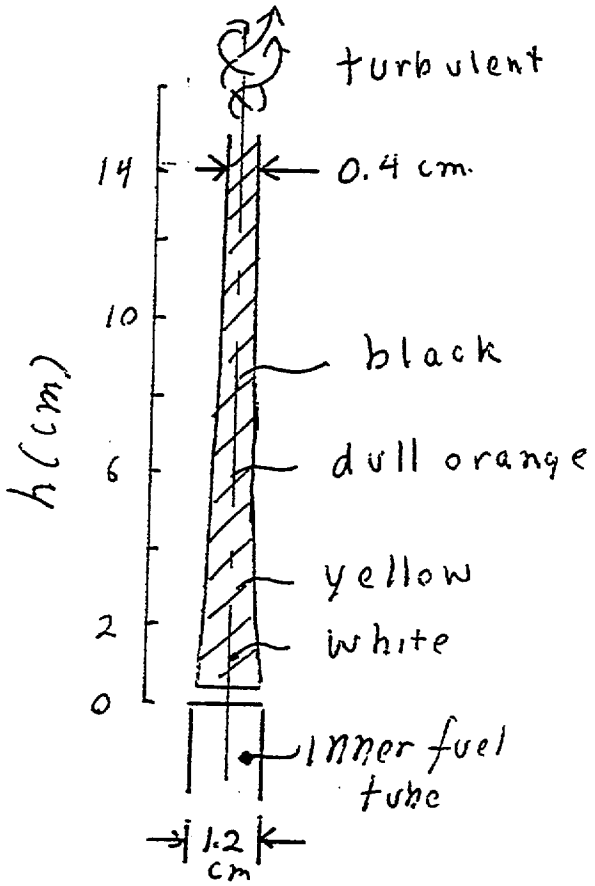

Fig. 1 Diagram of the C_2H_2 coannular diffusion flame.

C. Soot Sampling

1. Thermophoretic Sampling and TEM Analysis

Copper electron microscope grids with Formvar coating were placed on our "frog-tongue" probe device [2] designed after Dobbins and Megaridis [3]. This injects the grids into the flame for a residence time of 15msec. Grids were injected at a variety of heights above burner between 5.7 to 25.4cm. TEM micrographs at 14600X were taken and enlarged to 29200X. Figure 2 shows an example. These photographs were scanned into a PC in 16 levels of gray. Because of background noise, this was converted to a binary format using the eye as a judge of quality. Calibration of pixels to real sizes was performed. Programs were written to calculate projectional area and radius of gyration. Hundreds of clusters were analyzed. This whole analysis is similar to that which we have used earlier [2].

The average monomer size was 23nm (radius). Some clusters had a significantly smaller monomer size, representing a separate population. We don't know why.

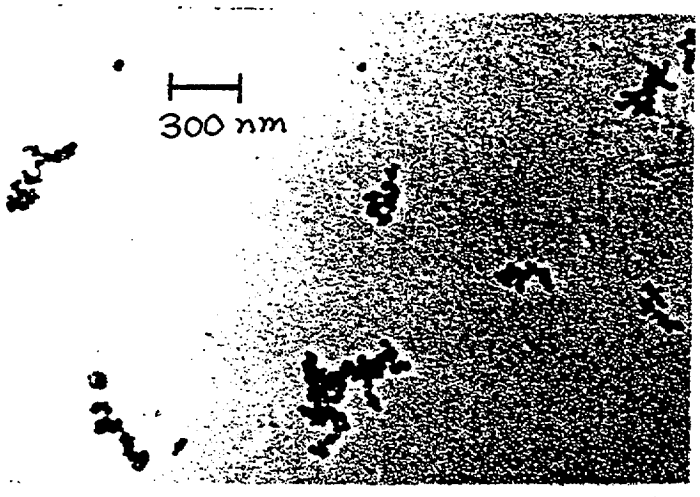

Fig. 2 TEM photograph of soot h=5.7cm.

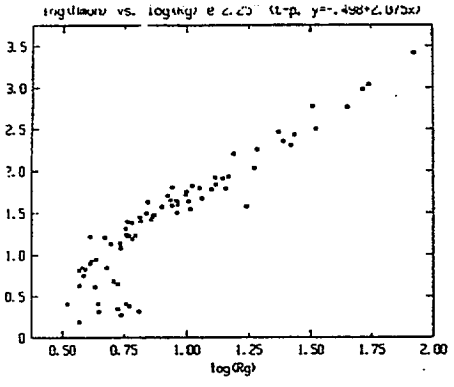

Fig. 3 A_{cl}/A_m vs. R_g (arb. units) for thermophoretically sampled soot $\langle R_g \rangle$~160nm, h=5.7cm.

For each cluster the radius of gyration R_g and the ratio of cluster area to a single monomer area A_{cl}/A_m was calculated. This ratio was then graphed versus R_g/a, an example of which is given in Fig. 3. These plots were linear, indicating fractility. Empirically [2,4] one expects the ratio of areas to be related to N the number of monomers per cluster by

$$N=(A_{cl}/A_m)^{1.09} \quad . \tag{1}$$

We then use

$$N=k_o(R_g/a)^{D_f} \quad . \tag{2}$$

to find D_f and k_o with results in Table I.

Table I

D_f and k_o for soot clusters sampled by thermophoresis.

Height Above Burner	D_f	k_o
5.7cm	1.92	0.79
7.6	1.77	1.20
9.5	1.82	1.02
11.4	1.79	1.07
15.2	2.01	1.14
25.4	1.71	1.50
Average	1.84±.11	1.12±0.23

These results, both D_f and k_o, agree very well with other measurements both by us and others on soot. k_o is less often studied but agrees well with a recent effort on our part [5].

We also graph mean R_g versus height above burner in Fig. 4. R_g increases with h as expected until $h \gtrsim 7.6$cm. This is where the flame turns black, nonluminous, see Fig. 1. Is our thermophoretic sampling breaking down?

This behavior and visual staring at the flame, which seemed to indicate there are bigger clusters, led us to try sampling by impaction rather than thermophoresis.

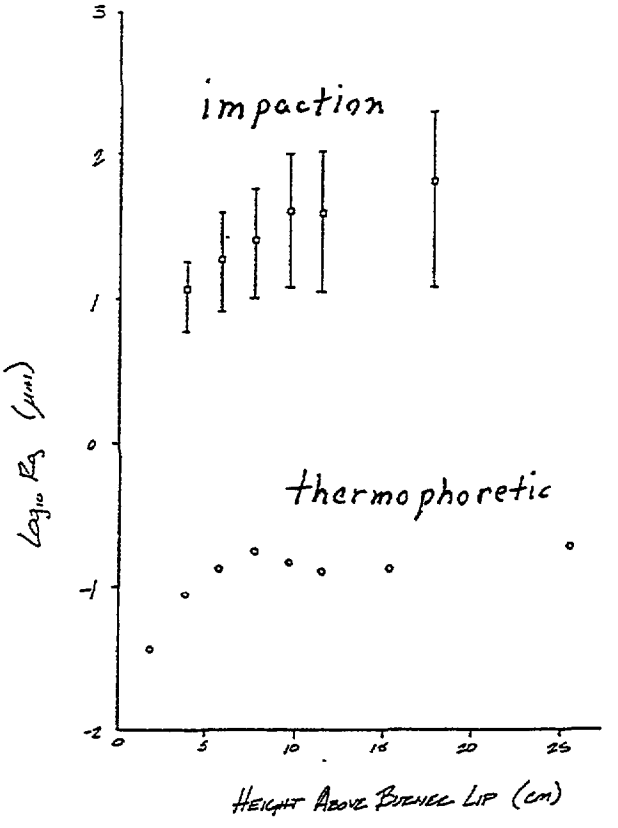

Fig. 4 $\langle R_g \rangle$ versus h for both thermophoretically and impaction sampled soot.

2. Impaction Sampling on Glass Microscope Slides

We used our frog-tongue sampling device again but with standard glass microscope slides (25x75mm) held perpendicular to the flow of the flame (i.e., horizontally). Thus impaction is the major collection scheme. Residence times were again 15 msec. The flame is perturbed a good deal, but some data is better than no data. Some clusters were visible to the naked eye. Samples were taken between 3.8 to 17.8cm above the burner.

An optical microscope was used to take photographs of the clusters. Obviously the ~23nm monomers are not resolved. The net magnification to the photographic print was 72X. Figure 5 shows an example. These were scanned into a PC and analyzed in the same manner as the TEM photographs.

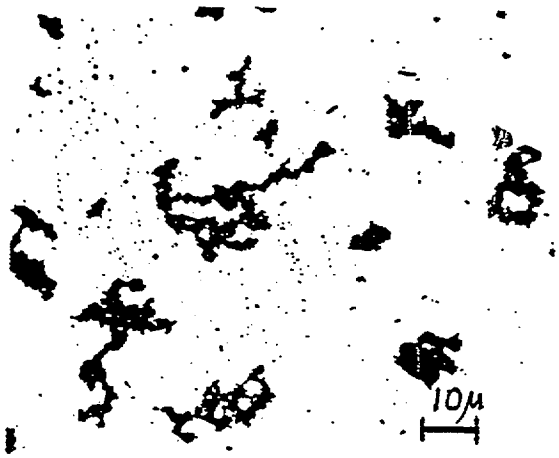

Fig. 5 Optical photograph of soot h=7.6cm.

The data set is weighted by the optical microscope observation range. Clusters much smaller than 10μ were not resolved, while those greater than ~1000μ=1mm were rare and too large to fit into the field of view.

Figure 4 shows mean R_g versus height above burner. This figure includes the TEM data and very little agreement is seen. We believe this is because both observation methods have their range of detectibility and these differ greatly. In fact its hard to imagine simultaneously observing clusters three orders of magnitude different in size. Three orders of magnitude is the ratio of the width of this page to the period at the end of this sentence. Also given scaling, as one changes the observation method i.e., the observation scale, one should see similar populations at different scales.

We also analyzed these optical clusters for their fractal dimension. A typical plot of A_{cl}/A_m vs. R_g is shown in Fig. 6. Table II gives D_f values.

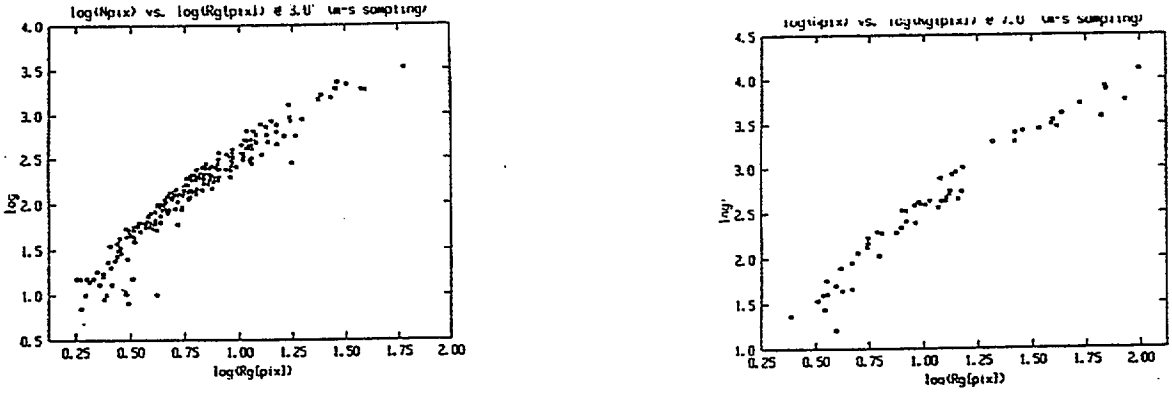

Fig. 6 A_{cl}/A_m vs. R_g (arb.units) for impaction sampled soot. 6a is for h=7.6cm, 6b for h=17.8cm.

Table II

Fractal Dimension of Optical Soot Clusters

Height Above Burner	D_f
3.8cm	1.54
5.7	1.68
7.6	1.75
9.5	1.78
11.4	1.77
17.8	1.82
Average	1.72±0.10

These values are within error smaller than the TEM cluster values, hence they are consistent.

3. Turbidity Measurements

Turbidity measurements were made with an argon ion beam at λ=488nm. The flame diameter was measured visually. Soot volume fractions were calculated assuming soot density uniformity and refractive index m=1.6+i0.6. Figures 7 and 8 give these results.

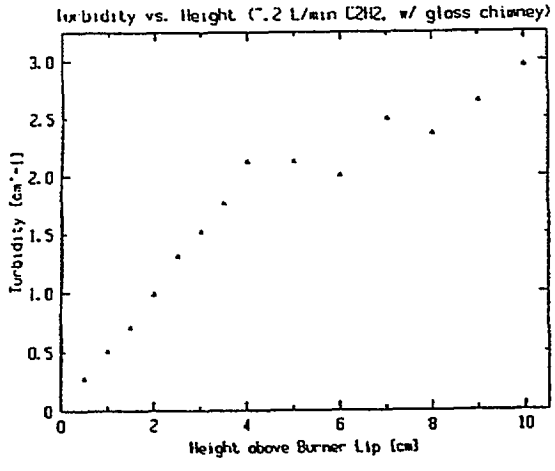

Fig. 7 Turbidity at λ=488nm versus h.

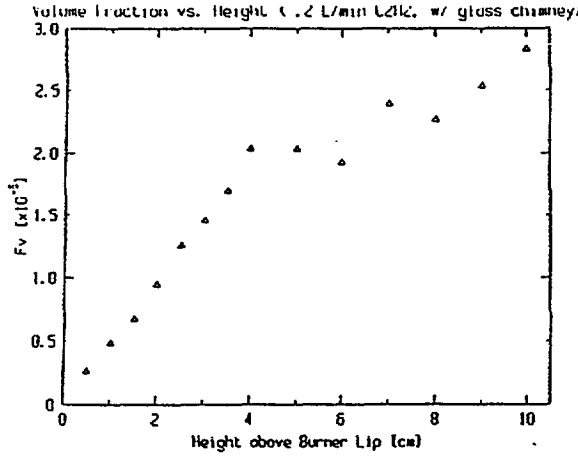

Fig. 8 Soot volume fraction versus h.

II. GELATION IN A FLAME

A fundamental question that motivates this work is, "How is it that 20nm monomers can aggregate in a few tens of millisecond to form ~2mm or larger clusters, a five order of magnitude change?" Visual observation of the large, low density flocs produced gave us the idea that perhaps these clusters grow until they touch--a gelation transition. Such a transition near the gel point would have kinetics faster than cluster-cluster aggregation.

The feasibility of this idea is seen in the following argument. We write the number of monomers in a cluster as

$$N \propto (R_g/a)^{D_f} \ . \tag{3}$$

The cluster volume is

$$V \sim R_g^3 \ , \tag{4}$$

thus the cluster monomer density is

$$n_{cl} \sim a^{-D_f} \, R_g^{D_f-3} \ . \tag{5}$$

The monomer density in the flame is related to the soot volume fraction f_v by

$$n_{fl} = 3f_v/4\pi a^3 \ . \tag{6}$$

Growing clusters will touch, i.e., fill all space when $n_{fl}=n_{cl}$. Solving for R_g under this condition we have

$$\begin{aligned} R_{g,gel} &\sim a\left(\frac{4\pi}{3f_v}\right)^{\frac{1}{3-D_f}} \\ &\sim a\left(\frac{4}{f_v}\right)^{\frac{1}{3-D_f}} \ . \end{aligned} \tag{7}$$

Our laser extinction measurements indicate $f_v \sim 10^{-5}$ to 10^{-6}. Our TEM work showed $a \approx 23$nm and an average D_f is ~1.8 then

$$R_{g,gel}(f_v=10^{-6}) \sim 7\text{mm} \tag{8a}$$

$$R_{g,gel}(f_v=10^{-5}) \sim 1\text{mm} \ . \tag{8b}$$

These sizes are readily obtained in our flame. Larger sizes are found on floors, tables, shelves, etc., throughout our lab!

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Post-Flame Soot
Award Number: 70NANB4H1652
Quarterly Report
March 1, 1995

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Although no overt advances have been made in the last quarter, reasonable progress has been made. A graduate student did start working on this project around January 15. To start him I'm having him reproduce some of our earlier work so that he can understand the fundamentals of what we know and how to apply it. He will soon begin new projects. Also, some work has been done checking out a slot diffusion burner built last summer. A reasonable amount of desk work has been accomplished including paper writing, literature reading, and experiment scheming. All is described in more detail below.

I. SLOT DIFFUSION BURNER FLAME

Last summer, Greg Roberts, an undergraduate physics major, built a two-slot diffusion burner and an xyz translation system for it. The fuel and oxidizer slots are parallel and each is 1cm by 5cm. These are inside a 10cm ID metal cylinder. Above the slot burner orifice, there is a box of tempered plate glass 12.5cm square. Roberts worked hard to achieve a uniform and stable diffusion flame. Important attributes to achieve this are: 1) a diffusing manifold for both fuel and oxidizer at the bottom of the slots, 2) a light screen on top of the slots, stabilizing metal "gulls" on each size above the slots, and N_2 sheath flow all contribute to flame stability, and 3) tempered glass is necessary to avoid breakage. It should fit tight to ensure flame stability.

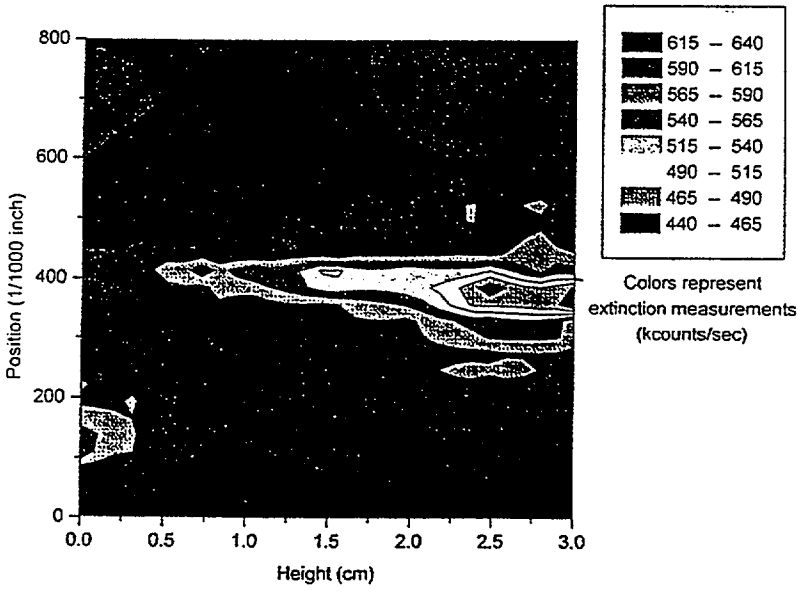

Fig. 1 Transmitted light intensity versus height above burner and position measured perpendicular to the plane of the septum between the fuel and oxidizer slots. Incident intensity is $I_o=630\pm10$ kcounts/sec. Septum at position=400. Flame was CH_4/O_2.

More recent turbidity and light scattering measurements have been made. The fuel was CH_4; the oxidizer was 0_2; and both flowed at 6.4 cm/s. Light scattering was harder than in premixed flames because of the narrowness of the flame above the slot combined with the slight lack of stability. Figure 1 shows a turbidity cross section of the flame and one can see this narrowness. Thus a slight wavering of the flame of only 0.3mm causes absorption and scattering random error. Figure 2 shows scattered intensity versus q, the scattering wave vector, for three different heights above burner. These data are not as smooth as those obtained from our premixed burner work due to the larger fluctuations from the small flame instability.

Our general result is that a working slot diffusion burner has been built. Light scattering is more difficult than for premixed burners due to the flame narrowness and a small, residual instability in the flame. We have not yet tried acetylene as a fuel or to look at post-flame soot. This is a possible future next step.

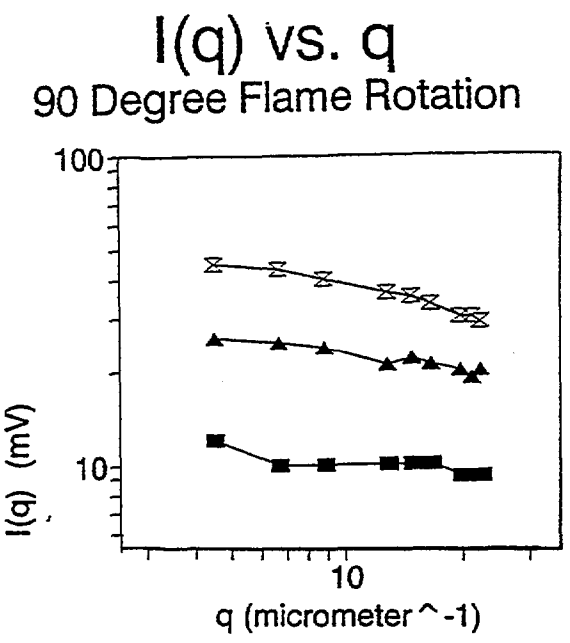

Fig. 2 Static structure factor for light scattered from a CH_4/O_2 slot diffusion flame.

II. PAPER ON POST-FLAME SOOT

We have written a first draft of a paper concerning post-flame soot from an acetylene diffusion flame. These results were discussed in the December 1, 1994 progress report. We hope to finish and submit this paper in about a month.

III. LARGE SOOT KINETIC STUDIES

In my last progress report I proposed the notion that the soot clusters would grow large enough to physically touch each other in the post-flame region. Rough calculations indicated that this would happen when the soot cluster size was $R_g \sim 1$mm. If so, we expect the DLCA growth kinetics, which occur early in the flame, should give way to gelation kinetics late in the flame when the clusters are this large.

Since then, I've spent a considerable amount of time deciding on how best to explore this large soot regime. I expect the kinetics to cross over when the average separation between clusters becomes comparable to the cluster diameter ($2R_g$). Note that for monomers the ratio of separation distance to diameter, d_{sep}/d_m, is $f_v^{-1/3}$, where f_v is the volume fraction of soot. For our acetylene diffusion flame $f_v \sim 10^{-5}$ so $d_{sep}/d_m \sim 46$.

Before I calculate $d_{sep}/2R_g$ for fractal clusters, it is very interesting to look at some recent literature concerning colloid aggregation when the clusters nearly touch [1-5]. First observed in 1992 [1], it has been shown that the light scattering structure factor for such a cluster-dense system is very similar to that observed in spinodal decomposition experiments [6]. A sketch of the structure factor for either system is shown in Fig. 3. The most important feature is the peak which gets larger and declines to small q with time, i.e., as the system coarsens. This peak is seen in the lab as a ring around $\theta=0$

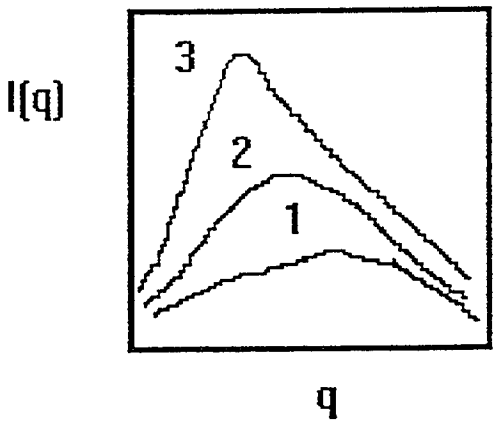

Fig. 3 Typical structure factor behavior which evolves with time for both cluster-dense aggregation and spinodal decomposition.

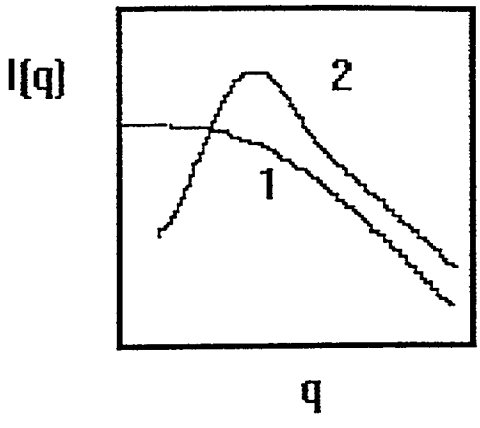

Fig. 4 Structure factor behavior for: curve 1, non-dense clusters, hence a single-cluster structure factor; curve 2, a cluster-dense system with a correlated structure factor.

which brightens and shrinks with time. One finds $q_{peak} \simeq 10^{+3} cm^{-1}$ to imply clusters or droplets on the order of 10^{-3}cm $= 10\mu$. However, it is important to realize the peak would not occur if the average separation between clusters or droplets wasn't 10μ as well. The peak is a result of the collective scattering from the system rather than independent cluster scattering.

These results, I believe, will be very relevant to our future work because $d_{sep}/2R_g \rightarrow 1$ in our flame. From our past work [7-9], I expect that when $d_{sep}/2R_g >> 1$ we will have the standard single particle structure factor, curve 1 in Figure 4. However as $d_{sep}/2R_g \rightarrow 1$ this should give way to a collective structure factor similar to those in Fig. 3 and represented by curve 2 in Fig. 4. I want to see if I can observe this crossover and measure R_g or q_{peak} as a function of time to determine the kinetics.

To plan the experiment I must know when $d_{sep}/2R_g \rightarrow 1$ in our sooty flame and to what values of q this will correspond. To calculate $d_{sep}/2R_g$ consider the following argument. The volume fraction is given by

$$f_v = \left(\frac{d_m}{d_{sep,m}} \right)^3 \qquad (1)$$

where d_m=dia. of monomer, $d_{sep,m}$=ave. separation of monomers. The total volume of the aerosol is

$$V_T = N_m \, d_{sep,m}^3 \, . \qquad (2)$$

For clusters the same total volume is

$$V_T = N_c \, d_{sep,c}^3 \qquad (3)$$

where N_c=number of clusters and $d_{sep,c}$=ave. separation between clusters. We also need

$$N \sim (R_g/a)^{D_f} \tag{4}$$

where N is the ave. number of monomers per cluster and $2a=d_m$. Now to calculate $d_{sep,c}/2R_g$ first set $V_T=V_T$, i.e., Eq.(2) equal Eq.(3)

$$N_c\, d_{sep,c}^3 = N_m\, d_{sep,m}^3 \ . \tag{5}$$

Then use $N_c=N_m/N$ so

$$d_{sep,c}^3 = N\, d_{sep,m}^3 \tag{6}$$

Now use Eqs.(1) and (4) to find

$$d_{sep,c}^3 = 8R_g^{D_f}\, a^{3-D_f}\, f_v^{-1} \tag{7}$$

to yield

$$\frac{d_{sep,c}}{2R_g} = (R_g/a)^{\frac{D_f-3}{3}}\, f_v^{-1/3} \ . \tag{8}$$

I have used Eq.(8) to calculate $d_{sep,c}/2R_g$ for $f_v=10^{-5}$ and a=25nm, very typical values. The results are shown in Fig. 5.

Figure 5 shows the average separation distance becomes comparable to the cluster diameter when the cluster R_g is $\sim 10\mu$ for $f_v=10^{-5}$. We collected bigger clusters than this so the correlated structure factor regime is definitely obtained in our flame. I estimate the smallest angle I can "easily" measure is 10^{-2} radian (1cm at 1m) which for $\lambda=0.5\mu$ light yields $q=1.2\times10^3$ cm^{-1} or $1/q=8\mu$. That is, I can observe sizes of $\sim 8\mu$ or smaller with light scattering. Thus I think we are on the edge of the correlated structure factor regime. Whereas, this peaked structure factor would be interesting to see, lets not forget the key measurement is the kinetics, and I don't expect the kinetics to crossover from DLCA to the proposed gel kinetics until $d_{sep,c}/2R_g$ is a few or less. Thus light scattering may only be able to see DLCA or at best the beginnings of the proposed new regime. So I need another technique.

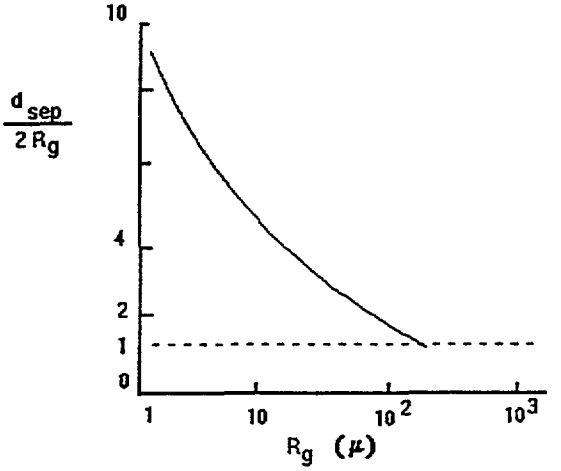

Fig. 5 Average cluster separation divided by cluster diameter versus cluster radius for a soot aerosol with $f_v=10^{-5}$, monomer radius a=25nm, and fractal dimension $D_f=1.75$.

I propose to use fast photography. For instance, for magnifying powers of 10 to 100x we should be able to see 100 to 10μ particles enlarged to ~1mm on a photographic negative. This is large enough to measure size directly and hence determine kinetics. Recall from the past report that thermophoretic and impaction sampling gave mean soot cluster sizes that differed by 2 1/2 orders of magnitude. Thus we need an in situ optical technique.

Since the particles are moving, we need flash photography. Commercial Xe arc lamps are available with line widths of ~1μsec. High in the flame, the flow rate is ~20cm/s; thus a particle would move ~0.2μ during such a flash. This is small compared to the minimum size of 10μ which we expect to observe photographically.

A commercial flash system involves a lamp, a power supply, a lamp holder, and misc. All for ~$3.5K. My budget does not hold this much equipment money, so when I'm sure this is what I want to do, I'll call and see if we can modify the budget.

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Post-Flame Soot

Award Number: 70NANB4H1652

Quarterly Report

June 1, 1995

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I. INTRODUCTION

Progress this quarter has been made on three fronts: 1) we solved a fractal morphology analysis problem for micrographs in which monomers are not resolved, and with this finished writing our paper on post-flame soot and submitted it for publication, 2) we have built a new scattering arrangement and diffusion burner for future experiments, and 3) we wrote a renewal proposal which was due June 1.

II. WORK ACCOMPLISHED

A. Morphology Analysis

As described in previous reports, we have analyzed the morphology of impaction sampled, optically viewed soot collected from an acetylene/air diffusion flame. This soot was captured on optical microscope slides and examined with an optical microscope at 72X. Because of this relatively low magnification, the individual monomers were not resolved. Despite this the morphology at this scale still looked fractal and a comparison of soot at two significantly different scales, Fig. 1, shows the remarkable self similarity of the fractal nature.

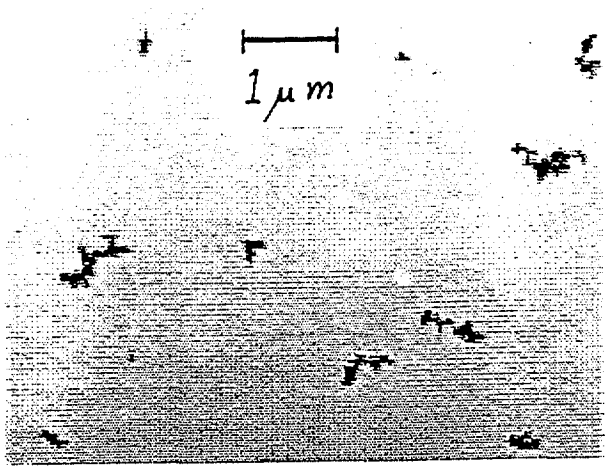

Fig. 1a TEM photograph of thermophoretically sampled soot at a height of h=7.6cm.

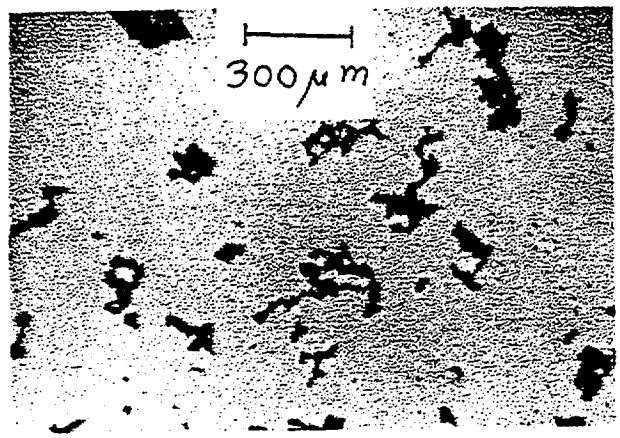

Fig. 1b Optical photograph of impaction sampled soot at a height of h=7.6cm.

Our analysis involved calculating the radius of gyration, R_g, of the digitized micrographs with a computer and determining the projected area of the cluster, A_c, from which the number of monomers per cluster was calculated using

$$N = (A_c/A_m)^{\alpha} \tag{1}$$

where $\alpha=1.09$. The N vs. R_g for an ensemble of clusters was graphed on a double log plot to yield straight lines, indicating fractals and adherence to

$$N = k_o(R_g/a)^{D_f} \tag{2}$$

where D_f is the fractal dimension and a is the monomer radius determined from the higher power (20800x) TEM micrographs. Both the TEM and optically viewed clusters yielded essentially the same D_f, but, to our surprise drastically different values of k_o; averages of $k_o=1.77$ for the TEM samples and $k_o=24.3$ for the optical samples. Herein was a dilemma; why the large difference in k_o?

After a length of time that I care not to admit, I finally resolved this dilemma. The cause of the discrepancy was due to the fact that the monomers were not resolved in the low power, optically viewed pictures. Because of this, a pixel, which represents the resolution limit of the micrograph, will contain many monomers. The number of monomers in a pixel determines whether the pixel will

be dark or bright; only the dark pixels will be included in the analysis for N. To account for this one must use the fractal nature of the monomeric particle arrangement and the ratio of effective pixel size to monomer size.

A quantitative description of this effect is given in our paper, submitted during this quarter, which I quote here.

To understand this problem consider the digitized image of a cluster at two different magnifications in Fig. 2. The resolution limit is set by the pixel size. For example, the cluster at magnification 1 might yield p_1=20nm/pixel whereas magnification 2 might yield p_2=10nm/pixel. The area (e.g., in nm^2) of the cluster is

$$A=n\ p^2 \tag{3}$$

where n is the number of pixels per cluster. If a higher magnification shows no new structure, then $A_1=A_2$, hence

$$n_2/n_1 = (p_1/p_2)^2 \ . \tag{4}$$

That is, because the scale is larger by a factor of p_1/p_2, there are more pixels in the image of the cluster in 2 by a factor of $(p_1/p_2)^2$. The exponent two results because the dimension of the plane is two.

Now consider the case where higher magnification reveals structure hidden at lower magnification as portrayed in Fig. 2. In this case the fractal nature of the projection of the cluster implies that Eq.(4) should be modified to

$$n_2/n_1 = (p_1/p_2)^{D_2} \tag{5}$$

where $D_2=D/\alpha$ is the fractal dimension of the cluster when projected into the two dimensional plane.

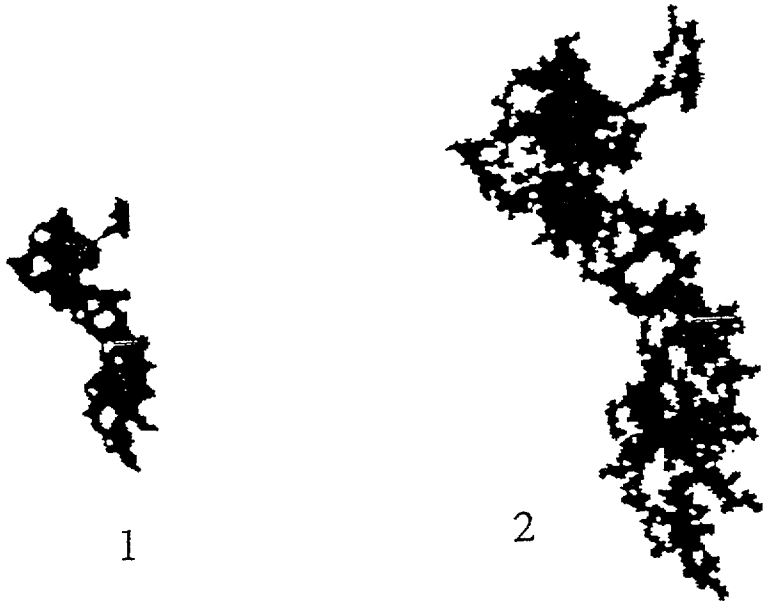

Fig. 2 Computer digitized image of a soot cluster at two magnifications differing by a factor of two. At magnification two additional structure is resolved.

From (3) and (5) we find

$$A_2/A_1 = (p_1/p_2)^{D_2-2} \tag{6}$$

then from Eqs.(1), (2) and (6) we find

$$k_{02}/k_{01} = (p_1/p_2)^{2\alpha-D} \ . \tag{7}$$

The scales for our optical and TEM clusters are p=3500 and 12.1nm/pixel, respectively. Thus using $\alpha=1.09$ and $D=1.76\pm0.05$ we find k_o(optical)/k_o(TEM)$=10.8\pm3.0$, where the approximate error is due to the error in D_f. k_o(optical) must be divided by this number to be compared to k_o(TEM), that is $(24.3\pm8.5)/(10.8\pm3)=2.25\pm1.0$. Within the large uncertainity, this agrees well with k_o(TEM)$=1.77\pm0.35$.

We feel this numerical comparison is only qualitatively correct since it assumes that hidden structure exists, hence the monomers are unresolved, at both the optical and TEM scales. This is not true for the TEM clusters; the monomer radius is a=23nm whereas p=12.1nm/pixel. Thus the monomer is roughly, but perhaps not completely, resolved. A better, but still qualitative, formulation is to compare p to a. When $p>>a$, the cluster is unresolved; and when $p<<a$, it is fully resolved,

and no correction should be made. Thus we modify Eq.(7) to

$$k_o = k_o(\text{unc.})\,(p/a)^{D-2\alpha},\ p/a \geq 1. \qquad (8)$$

Equation (8) gives the "true", corrected k_o value from the unresolved and uncorrected value k_o(unc.). We consider again our optical clusters with p=3500 nm/pixel and a=23nm and find a correction factor of $(p/a)^{D-2\alpha}=0.12\pm0.03$. (Note that the inverse of 0.12 is 8.3 to compare to the correction of 10.8 above.) This correction applied to the average uncorrected k_o(unc.) in Table 2, below, for the optical clusters yields $k_o=2.9\pm1.0$. This value is considerably larger than the TEM value of 1.77 ± 0.35 but still within experimental error.

Table 1
D_f and k_o for Soot Clusters Sampled by Thermophoresis and Viewed by TEM

Height Above Burner	D_f	k_o
5.7cm	1.92	1.36
7.6	1.77	2.00
9.5	1.82	1.69
11.4	1.79	1.73
15.2	2.01	1.42
25.4	1.71	2.39
Average	1.84 ± 0.11	1.77 ± 0.35

Table 2
D_f, Uncorrected k_o, and k_o Corrected for the Nonresolved Monomer at the Viewing Magnification, for Soot Clusters Sampled by Impaction and Viewed Optically

Height Above Burner	D_f	k_o(unc.)	k_o
5.7	1.68	37.8	4.53
7.6	1.75	25.9	3.10
9.5	1.78	21.1	2.53
11.4	1.77	21.8	2.62
17.8	1.82	15.1	1.81
Average	1.76 ± 0.05	24.3 ± 8.5	2.92 ± 1.0

Resolution of this problem allowed us to finish our paper which we summarize below.

B. Summary of our Paper, "Morphology of Macroscopic Post-Flame Soot," by Sorensen and Feke, submitted to Combustion and Flame.

We studied the morphology of soot collected from a laminar acetylene diffusion flame in still air. The burner was simply a 0.9cm ID tube through which acetylene flowed at a rate of $3.2cm^3$/sec. Soot was sampled both thermophoretically and via impaction, both using a sampling device that held the collection TEM grid or microscope slide in the flame for 15 msec. The thermophoretic samples were viewed with a TEM at 20800x magnification. The impaction samples were viewed with an optical microscope at 72x. Photographs were digitized and analyzed with a computer. Over 1000 soot clusters were analyzed to obtain N, the number of monomers per cluster, a, the monomer radius, and R_g, the cluster radius of gyration. From these measurements the fractal dimension D_f and the prefactor k_o were obtained by fitting to Eq.(2).

We found the impaction sampled, optically viewed samples had a mean R_g 2 1/2 orders of magnitude greater than the thermophoresis sampled, TEM viewed mean R_g. This discrepancy appears to be related to sampling bias, impaction tends to collect larger particles, and observation scale, 20800x is 2 1/2 orders of magnitude larger than 72x. This issue is not yet resolved, so we will pursue it in our future work.

Morphological studies were very successful. Figures 1a and 1b above show micrographs that are approximately 2 1/2 orders of magnitude different in scale yet note that the general morphology of the clusters is the same. Our largest soot clusters were nearly 1mm across ($R_g \sim 0.4$mm). The range in R_g was four orders of magnitude; in N it was several orders of magnitude. We found that throughout this great range the morphology was the same: fractal with $D_f = 1.80 \pm 0.1$ and $k_o \simeq 2.3 \pm 0.6$. Such a description was one of the goals of our proposal. Tables 1 and 2 show our results and Fig. 3, which plots N vs. R_g, demonstrates the large range of similarity.

These results are important because they study soot two orders of magnitude larger (in R_g) than any previous work. They establish that the same morphology holds from clusters of a few

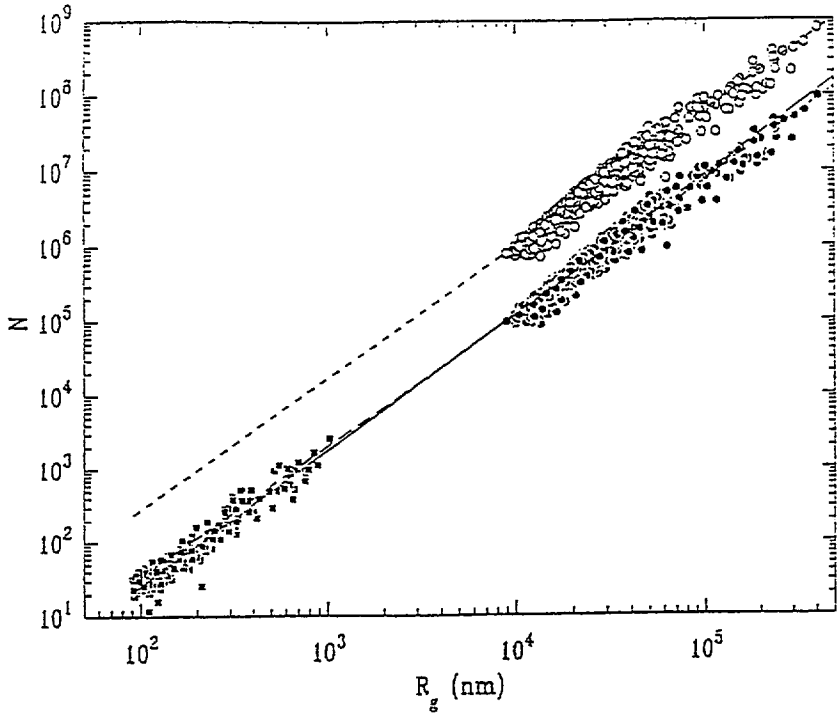

Fig. 3 Number of monomers per cluster versus cluster radius of gyration for both thermophoretically sampled, TEM viewed soot (closed squares) and impaction sampled, optically viewed soot (circles). This is a composite plot of all soot obtained at all heights above burner. For the optically viewed soot the open circles are uncorrected, the closed circles are corrected by multiplying by 0.12. The lines are fits to Eq.(2) which yield D_f=1.84 and k_o=1.73 for the squares and D_f=1.78 and k_o=2.44 for the closed circles.

monomers up to clusters of 100 million monomers! Both D_f and k_o, which we measured over this vast range of sizes, are key variables for future optical and kinetic characterization. Finally, our results strongly imply that Diffusion Limited Cluster Aggregation (DLCA) is the kinetics of formation upto this large size range.

B. New Burner Arrangement

Our previous coannular diffusion burner was used in place of our McKenna premixed burner on the same optical table. Thus only one burner could operate at a time. To alleviate this congestion we have dedicated a separate optical table, Ar^+ laser, and detector to the diffusion burner. Furthermore, we have rebuilt the burner and built a new goniometer to be used with it.

The rebuilt burner is similar to that described above but has provisions for either a cylindrical 4" dia. chimney or a rectangular 4"x4" chimney. The rectangular chimney will be better suited for

small angle scattering because cylindrical tubes have glare spots at small angle. We also have significantly improved our withdrawal arrangement to remove soot from the lab.

We are currently testing our burner with acetylene. A problem is evident in that the flame and especially the black post-flame, laminar flowing soot aerosol wavers somewhat on time sales of tenths to a few seconds with amplitudes on the order of as much as a few millimeters. This would make light scattering impossible, although fast photograph would still work. Attempts to alleviate this wavering with the coannular flow have so far been unsuccessful, but more efforts will be made. A promising avenue to achieve stability is that we have noticed that if a disk of metal with a hole ca. two times the diameter of the aerosol flow (i.e., ca. 10 mm) is placed so that the aerosol flows through the hole, the flow of the aerosol can be pushed sideways by moving the disk a few mm. This implies such a disk can control the flow. Perhaps a series of disks or one disk near the scattering volume will work to stabilize the flow. We shall see.

Post-Flame Soot

Award Number 70NANB4H1652

Quarterly Report
September 1, 1995

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Progress was made during the past quarter in two areas: construction of long working distance microscope and structure factor measurements from an acetylene in air diffusion flame.

1. The Microscope

We would like to make direct, *in situ* observations of soot with high speed photography. To do this we need a long working distance microscope. We constructured such a microscope with a working distance of 5-6" and a magnifying power variable between 10 and 90x. The layout is drawn in Fig. 1.

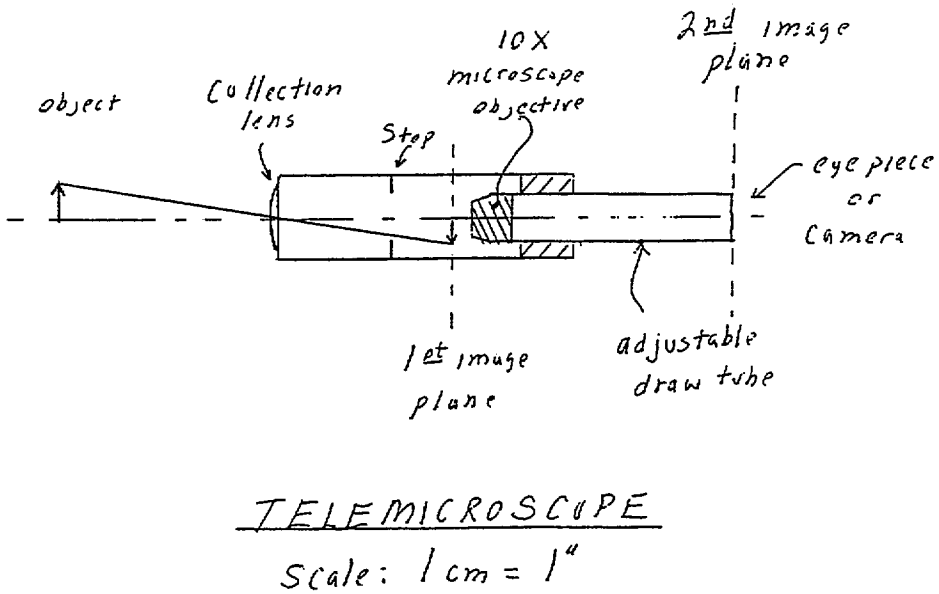

Figure 1 Telemicroscope capable of 10-90 power at ~5-6 in working distances.

We have tested this microscope on stationary objects both visually and photographically and it works quite well. The next step is to get a microsecond flash lamp. Unfortunately, this will have to wait since such a lamp, housing, and supply will cost ca. $4,000.

2. The Structure Factor of an Acetylene in Air Diffusion Flame

At the end of the last period, we were just finishing construction of a burner and goniometer arrangement for structure factor, S(q), measurements from an C_2H_2 diffusion flame. At that time, we had problems with flame and aerosol stability. The soot stream, luminous or not, wavered slightly, 1≤mm, and this caused an unexceptable fluctuation in the scattered light. We found that a wire screen with a ~ 1cm hole could be used to stabilize the flame. If the flame passes through the hole, the flame appears to try to keep a buffer of clear air ~ 2mm wide between it and the edge of the hole. Thus the screen can be used to hold the flame still.

This significantly improved flame stability, but more was needed. Room air currents caused flame flicker. To eliminate these the flame was contained in variable length, 4" I.D. glass tubes. These were capped by the screens. The air inlet at the bottom of the burner had to be fenced off with screen material to stop air currents. The final arrangement is drawn in Fig. 2.

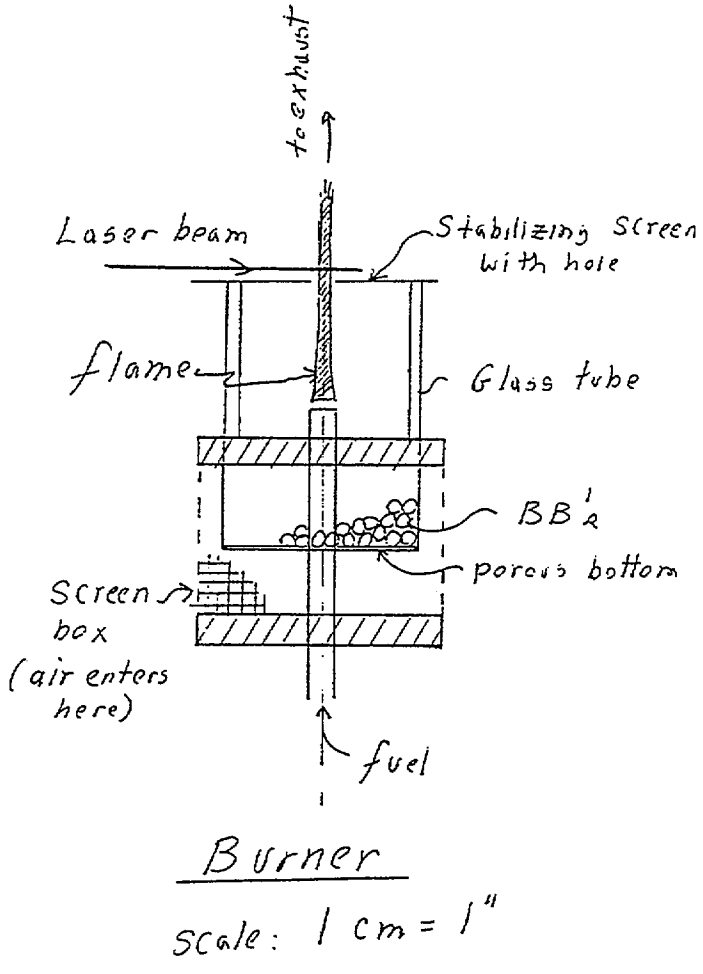

Figure 2 Drawing of burner arrangement.

Light scattering is performed ~1/2 cm above the screen. Note there are no glass walls hence no problems with wall spots. Lack of a chimney is not a problem because the exhaust hood is sufficient to collect the thin (~5mm) stream of soot. Variable length tubes allow for different heights above burner. With this burner, we have measured S(q) down to a 1° scattering angle.

We have obtained quite a bit of S(q) data which are beginning to tell an interesting story. Figure 3 shows S(q) for different heights above the burner for a fairly low flow rate of 28 ml/min. Note that the onset of smoke released from the flame is 24 ml/min. These S(q) have the expected shape for independent fractal aggregates. The fractal dimension is the negative slope of the large q regime and we find D=1.8. Guinier analysis was used to determine the cluster radius of gyration, R_g. Remarkably R_g varies only slightly with h; h=3cm, R_g=0.40μ; h=18cm, R_g=0.45μ.

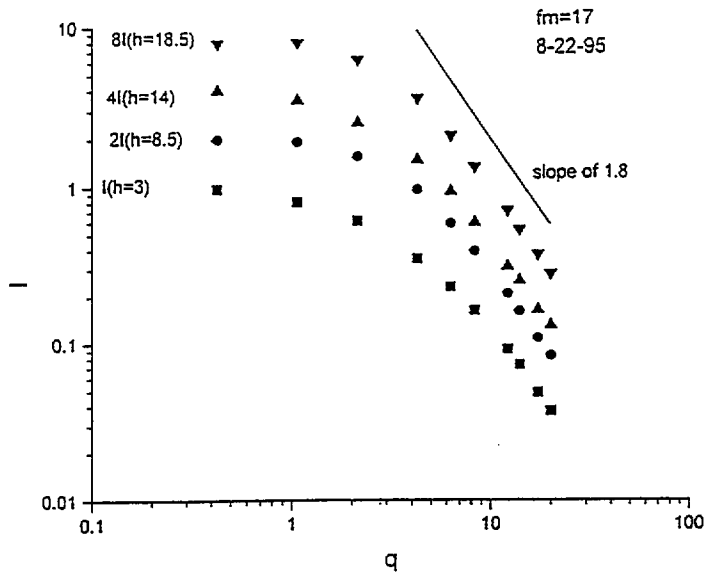

Figure 3 Normalized intensity versus q in $(\mu m)^{-1}$ for C_2H_2 diffusion flame.

Figure 4 shows how S(q) changes as the flow rate increases at constant h. All curves show the same large q behavior to yield D=1.8. The behavior of R_g is interesting as shown below

f(ml/min)	26	28	30
$R_g(\mu m)$	0.23	0.45	>5

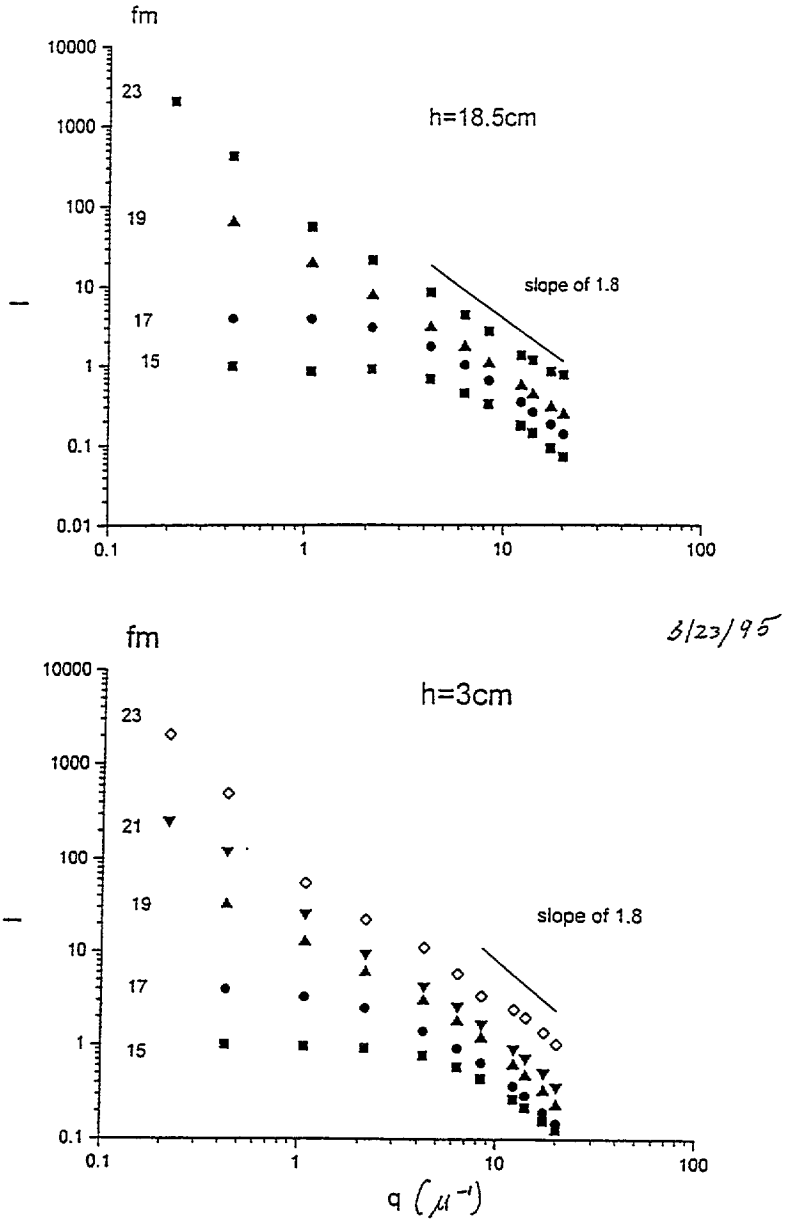

Figure 4 Intensity versus q in $(\mu m)^{-1}$ at a height of either 3cm or 18.5cm. Intensity at fm=15, which corresponds to a flow rate of 26 ml/min, is normalized to unity at the smallest q value. Other fm value are multiplied by factors to separate the spectra.

Obviously some rapid change is occurring between 28 and 30 ml/min.

Figure 5 shows the largest flow rate yet studied at various heights h. No Guinier regime is seen even for the smallest q which represents θ=1.0°. The general slope trend implies D=1.8. Note, however, the reproducible dimple in the spectra, marked by the arrow. What is this? We've checked our calibrations, angles etc. and are beginning to think that this is a real feature of S(q). Numerical calculations can reproduce this shape if two populations of soot exist with an order of magnitude different average R_g.

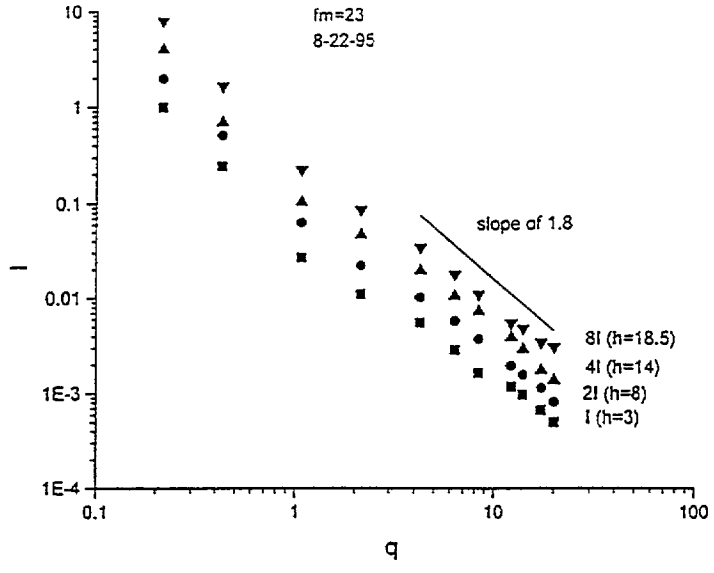

Figure 5 Intensity versus q in $(\mu m)^{-1}$ for fm=23 which corresponds to a flow rate of 35.5 ml/min.

We are pleased with our results because they are reproducible and indicate further work. We will study R_g versus h for h<3cm to fill out this dependency. Why does R_g increase so little at large h? Laser doppler measurements will give us time scales to see if there is adequate time for aggregation to occur.

We will also study the essentially catastrophic change in R_g between flow rates 28 and 30 ml/min. More data is needed between this rates. Why isn't this change at the same point as the onset of smoke emission from the flame? Are these points related?

Another, more prosaic fuel will be studied. Perhaps C_2H_4 or CH_4. C_2H_2 makes such large quantities of soot that I want to see if it is in fact unusual.

Finally, I may squeeze the budget and get a CCD array to allow us to go to 0.1° (for an R_g ~ 50nm). A look at Figs. 4 or 5 show that's where the action is.

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POST-FLAME SOOT

CONTRACT OR GRANT NUMBER
Grant no. 70NANB4H1652

TYPE OF REPORT AND/OR PERIOD COVERED
Final Report/September 1994 - December 1995

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The smoke agglomerates produced by a co-annular diffusion flame with acetylene fuel were characterized by sampling/microscopy and by light scattering measurements. Particles were sampled at various heights above the flame using both thermophoretic sampling and impaction. Transmission electron microscopy was used for the smaller agglomerates obtained by thermophoretic sampling and optical microscopy was used for analysis of particles as large as .4 mm in diameter collected by impaction. The number of primary spheres was estimated from the projected area of the agglomerate and the primary sphere size. The fractal analysis extended over four orders of magnitude in the radius of gyration - the widest range studied for smokes. The fractal dimension and the prefactor were determined for smoke collected for a range of heights above the flame. The structure factor measurements were performed for angles ranging from 1° to 150° as a function of height and fuel flow. No Guinier regime was observed at a flow rate of 30 ml/min. Modeling results suggest that the slight dip in the structure factor measurements might result from intercluster scattering. A condition for the transition from Brownian agglomeration to gelation is derived.

KEY WORDS (MAXIMUM OF 9; 28 CHARACTERS AND SPACES EACH; SEPARATE WITH SEMICOLONS; ALPHABETIC ORDER; CAPITALIZE ONLY PROPER NAMES)
acetylene; diffusion flames; flame research; light scattering; smoke; soot

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